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## **(54) NONAQUEOUS ELECTROLYTIC SOLUTION SECONDARY BATTERY AND NONAQUEOUS ELECTROLYTIC SOLUTION FOR USE IN THE SAME**

### **(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a nonaqueous electrolytic solution secondary battery having a superior charging/discharging efficiency and storage characteristics.

**SOLUTION:** An electrolytic solution composed of a nonaqueous solvent in which lithium salt is dissolved and further containing fluorinated nitrile compounds is used for the nonaqueous electrolytic solution secondary battery.

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## CLAIMS

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### [Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery which are a metal lithium, a lithium alloy or the negative electrode that contains occlusion and the ingredient which can be emitted for a lithium, the positive electrode which contains occlusion and the ingredient which can be emitted for a lithium, and a nonaqueous electrolyte rechargeable battery which contains in a non-aqueous solvent at a list the electrolytic solution which comes to dissolve lithium salt, and is characterized by containing the nitryl compound fluorinated in the electrolytic solution.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 characterized by choosing the fluorinated nitryl compound from the group which consists of a fluoro acetonitrile, alpha-fluoro propionitrile, and beta-fluoro propionitrile.

[Claim 3] The nonaqueous electrolyte rechargeable battery according to claim 1 or 2 with which the nitryl compound with which it was fluorinated in the electrolytic solution is characterized by occupying 0.01 - 10% of the weight of the electrolytic solution.

[Claim 4] The nonaqueous electrolyte rechargeable battery according to claim 1 to 3 characterized by being the mixed solvent with which what was chosen from the group which the lactone compound or annular carbonate of carbon numbers 3-9 occupies more than 20 capacity %, and a non-aqueous solvent becomes from the lactone compound, annular carbonate, and chain-like carbonate, chain-like ether, and chain-like carboxylate of carbon numbers 3-9 including this occupies more than 70 capacity %.

[Claim 5] Lithium salt LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>), The nonaqueous electrolyte rechargeable battery according to claim 1 to 4 characterized by being chosen out of the group which consists of LiPF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, LiBF<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>, and LiBF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>.

[Claim 6] The nonaqueous electrolyte rechargeable battery according to claim 1 to 5 characterized by occlusion and the negative-electrode ingredient which can be emitted being carbon materials whose d values of a lattice plane [ in / for a lithium / an X diffraction ] (002nd page) are 0.335-0.34nm.

[Claim 7] The nonaqueous electrolyte used for a nonaqueous electrolyte rechargeable battery according to claim 1 to 6.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to a nonaqueous electrolyte rechargeable battery. By using a detailed specific nonaqueous electrolyte, charge-and-discharge

effectiveness is raised and it is related with the nonaqueous electrolyte rechargeable battery which is excellent in charge-and-discharge effectiveness and a preservation property also under the elevated temperature.

[0002]

[Description of the Prior Art] development of the lithium secondary battery which has a high energy density with lightweight-izing of an electric product in recent years, and a miniaturization -- before -- furthermore, it is wished and the improvement of a cell property is also demanded with expansion of Field of application of a lithium secondary battery. The nonaqueous electrolyte rechargeable battery using occlusion and the compound which can be emitted is proposed in the lithium ion which said to current and a positive electrode as the metallic-oxide salt of LiCoO<sub>2</sub>, LiMnO<sub>2</sub>, and LiNiO<sub>2</sub> grade, and was said to the negative electrode as metallic-oxide ingredients, such as carbon materials, such as corks besides a metal lithium, an artificial graphite, and a natural graphite, and Sn, Si.

[0003] However, in these lithium secondary batteries, it is known that disassembly of the solvent of the electrolytic solution will take place on a positive electrode and/or a negative electrode, and this causes [ of charge-and-discharge effectiveness or a preservation property ] a fall. For example, in the nonaqueous electrolyte rechargeable battery which was independent about the graphite, or mixed the lithium with occlusion and other ingredients which can be emitted, and was used as the negative electrode, if the electrolytic solution which uses as the main solvent the propylene carbonate used with a lithium primary cell, being fond generally is used, the decomposition reaction of a solvent will advance violently on a graphite front face, and the occlusion of the smooth lithium to a graphite and emission will become impossible.

[0004] On the other hand, since there is little such decomposition, ethylene carbonate is used abundantly as a main solvent of the electrolytic solution of a nonaqueous electrolyte rechargeable battery. However, about ethylene carbonate, in order that the electrolytic solution may cause [ in / as a main solvent / a charge-and-discharge process ] small quantity [ every ] decomposition in an electrode surface, there is a problem that decline in charge-and-discharge effectiveness takes place.

[0005]

[Problem(s) to be Solved by the Invention] In a nonaqueous electrolyte rechargeable battery, disassembly of the electrolytic solution is suppressed to the minimum, charge-and-discharge effectiveness is high, and in order to realize the thing of a high energy consistency which excelled [ bottom / of an elevated temperature ] in the preservation property, making a protective coating with sufficient stability generate is proposed with lithium ion permeability on the electrode, and the electrolytic solution containing the ingredient which makes such a protective coating generate is desired. This invention tends to meet such a request.

[0006]

[Means for Solving the Problem] Since the coat with sufficient stability generated from the time of early charge efficiently with lithium ion permeability to the electrode surface and disassembly of too much electrolytic solution was controlled by using what contains the fluorinated nitryl compound as the electrolytic solution of a nonaqueous electrolyte rechargeable battery, this invention person etc. finds out that charge-and-discharge effectiveness and a preservation property may be raised, and came to complete this

invention.

[0007] That is, this invention is characterized by using the thing containing the nitril compound fluorinated as the electrolytic solution in a metal lithium, a lithium alloy or the negative electrode that contains occlusion and the ingredient which can be emitted for a lithium, the positive electrode which contains occlusion and the ingredient which can be emitted for a lithium, and the nonaqueous electrolyte rechargeable battery which contains in a list the electrolytic solution which comes to dissolve lithium salt at a non-aqueous solvent.

[0008]

[Embodiment of the Invention] As what makes the subject of the non-aqueous solvent of the electrolytic solution used by this invention, although annular carbonate and chain-like carbonate, a lactone compound, chain-like ester, cyclic ether, the chain-like ether, a sulfur-containing organic solvent, etc. are known as a solvent of the nonaqueous electrolyte for rechargeable batteries, from inside, it can choose suitably and they can be used. These solvents may be used independently, or two or more kinds may be mixed and they may be used. As a suitable solvent, the annular carbonate and lactone compound, the chain-like carbonate, the chain-like carboxylate, and the chain-like ether of 3-9 are mentioned for a carbon number. Some of desirable examples of these solvents are shown below.

[0009] Annular carbonate: Ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, vinyl ethylene carbonate. Ethylene carbonate and propylene carbonate are more desirable also in these. Lactone compound: Gamma-butyrolactone, gamma-valerolactone, delta-valerolactone. Gamma-butyrolactone is more desirable especially.

[0010] Chain-like carbonate : Dimethyl carbonate, diethyl carbonate, G n-propyl carbonate, diisopropyl carbonate, n-propyl isopropyl carbonate, Di-n-butyl carbonate, diisobutyl carbonate, G t-butyl carbonate, n-butyl isobutyl carbonate, n-butyl-t-butyl carbonate, Isobutyl-t-butyl carbonate, ethyl methyl carbonate, Methyl-n-propyl carbonate, n-butyl methyl carbonate, Isobutyl methyl carbonate, t-butyl methyl carbonate, ethyl-n-propyl carbonate, n-butyl ethyl carbonate, isobutyl ethyl carbonate, t-butyl ethyl carbonate, n-butyl-n-propyl carbonate, isobutyl-n-propyl carbonate, t-butyl-n-propyl carbonate, n-butyl isopropyl carbonate, isobutyl isopropyl carbonate, t-butyl isopropyl carbonate. Dimethyl carbonate, diethyl carbonate, and ethyl methyl carbonate are more desirable also in these.

[0011] Chain-like carboxylate: Methyl acetate, ethyl acetate, n propyl acetate, acetic-acid-isopropyl, n-butyl acetate, isobutyl acetate, acetic-acid-t-butyl, methyl propionate, ethyl propionate, propionic-acid-n-propyl, propionic-acid-isopropyl, propionic-acid-n-butyl, propionic-acid isobutyl, propionic-acid-t-butyl. Ethyl acetate, methyl propionate, and ethyl propionate are more desirable also in these.

[0012] Chain-like ether: Dimethoxymethane, 1, 2-dimethoxyethane, diethoxy methane, 1, 2-diethoxy ethane, ethoxy methoxy methane, 1-ethoxy-2-methoxyethane.

Dimethoxyethane and diethoxy ethane are more desirable also in these.

Cyclic ether; a tetrahydrofuran, tetrahydropyran, 1, 3-dioxolane, 1, 3-dioxane, 1,4-dioxane.

Sulfur-containing organic solvent; a tetramethylen sulfone, 3-methyl tetramethylen sulfone, a tetramethylen sulfoxide, 1, 3-propane sultone, 1 and 3, 2-dioxa thio run -2, 2-

dioxide.

The lactone compound or annular carbonate of carbon numbers 3-9 of especially a desirable thing is the mixed solvent with which what was chosen from the group which occupies more than 20 capacity %, and consists of lactone compound, annular carbonate, and chain-like carbonate, chain-like ether, and chain-like carboxylate of carbon numbers 3-9 including this occupies more than 70 capacity % as a non-aqueous solvent of the electrolytic solution used by this invention.

[0013] Lithium salt is used as a solute of the electrolytic solution used by this invention. Although it is known that it can use as a solute of nonaqueous electrolyte as lithium salt, it can choose from inside suitably and can use. When the some are illustrated, inorganic lithium salt:LiPF<sub>6</sub>, LiAsF<sub>6</sub> and LiBF<sub>4</sub>, the inorganic fluoride salt of LiAlF<sub>4</sub> grade, The organic sulfonate of fault halogen acid salt organic lithium salt:LiCF<sub>3</sub>SO<sub>3</sub> grades, such as LiClO<sub>4</sub>, LiBrO<sub>4</sub>, and LiIO<sub>4</sub>, Perfluoroalkyl sulfonic-acid imide salts, such as LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub>, and LiN(CF<sub>3</sub>SO<sub>2</sub>)(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>), The perfluoroalkyl sulfonic-acid methide salt of LiC(CF<sub>3</sub>SO<sub>2</sub>)<sub>3</sub> grade, LiPF<sub>5</sub> LiPF<sub>2</sub>(CF<sub>3</sub>)<sub>4</sub> LiPF<sub>3</sub>(CF<sub>3</sub>)<sub>3</sub> LiPF<sub>2</sub>(CF<sub>3</sub>)<sub>4</sub> LiPF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub> LiPF(C<sub>2</sub>F<sub>5</sub>)<sub>5</sub> LiPF<sub>2</sub>(n-C<sub>3</sub>F<sub>7</sub>)<sub>4</sub>, LiPF<sub>3</sub>(n-C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, LiPF(iso-C<sub>3</sub>F<sub>7</sub>)<sub>5</sub>, LiPF<sub>2</sub>(iso-C<sub>3</sub>F<sub>7</sub>)<sub>4</sub>, LiPF<sub>3</sub>(iso-C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, LiB(CF<sub>3</sub>)<sub>4</sub> and LiBF(CF<sub>3</sub>)<sub>3</sub>, LiBF<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>, LiBF<sub>3</sub>(CF<sub>3</sub>), (n-C<sub>3</sub>F<sub>7</sub>) LiB(C<sub>2</sub>F<sub>5</sub>)<sub>4</sub>, LiBF(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, LiBF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub>, LiBF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>), LiB(n-C<sub>3</sub>F<sub>7</sub>)<sub>4</sub>, LiBF(n-C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, LiBF<sub>2</sub>(n-C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>, LiBF<sub>3</sub>(n-C<sub>3</sub>F<sub>7</sub>), LiB(iso-C<sub>3</sub>F<sub>7</sub>)<sub>4</sub>, LiBF(iso-C<sub>3</sub>F<sub>7</sub>)<sub>3</sub>, LiBF<sub>2</sub>(iso-C<sub>3</sub>F<sub>7</sub>)<sub>2</sub>, LiBF<sub>3</sub>(iso-C<sub>3</sub>F<sub>7</sub>), etc., Inorganic fluoride salt fluoro phosphate which permuted some fluorines by the perfluoroalkyl radical, and fluorine-containing organic lithium salt of perfluoroalkyl.

[0014] LiPF<sub>6</sub>, LiBF<sub>4</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, LiN(C<sub>2</sub>F<sub>5</sub>SO<sub>2</sub>)<sub>2</sub> and LiN(CF<sub>3</sub>SO<sub>2</sub>)(C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>), LiPF<sub>3</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>3</sub>, LiBF<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>, and LiBF<sub>2</sub>(C<sub>2</sub>F<sub>5</sub>)<sub>2</sub> are more desirable also in these. In addition, these solutes may mix two or more kinds, and may be used. As for the lithium salt mol concentration of the solute in the electrolytic solution, it is desirable that it is 0.5-3 mols/l. If concentration is too low, the conductivity of the electrolytic solution is too low, and since viscosity rises, and conductivity falls and a deposit at low temperature becomes easy to take place even if concentration is too high conversely preferably, it falls and is not desirable [ the engine performance of a cell ].

[0015] In addition to an above-mentioned solvent and an above-mentioned solute, the electrolytic solution used by this invention contains the compound of the structure where the piece was further permuted by the fluorine atom at least of the hydrogen atom of the fluorinated nitryl compound, i.e., the hydrocarbon compound permuted by the cyano group. The substituent of further others may exist in this compound. The following is mentioned as a nitryl compound permuted by the suitable fluorine atom to use by this invention.

[0016] Chain-like nitryl compound; A fluoro acetonitrile, a difluoro acetonitrile, A trifluoro acetonitrile, alpha-fluoro propionitrile, beta-fluoro propionitrile, alpha and alpha-difluoro propionitrile, alpha, beta-difluoro propionitrile, beta and beta-difluoro propionitrile, alpha and alpha, beta-trifluoro propionitrile, alpha, beta, and beta-trifluoro propionitrile, beta and beta, beta-trifluoro propionitrile, alpha, alpha and beta, beta-tetrafluoro propionitrile, alpha, beta and beta, beta-tetrafluoro propionitrile, pentafluoro propionitrile [0017] Alicyclic nitryl compound; 2-fluoro cyclohexane carbonitrile, 3-fluoro cyclohexane carbonitrile, 4-fluoro cyclohexane carbonitrile, 2, 3-difluoro cyclohexane carbonitrile, 2, 4-difluoro cyclohexane carbonitrile, 2, 5-difluoro

cyclohexane carbonitrile, 2, 6-difluoro cyclohexane carbonitrile.

Aromatic series nitryl compound; 2-fluorobenzo nitril, 3-fluorobenzo nitril, 4-fluorobenzo nitril, 2, 3-difluorobenzo nitril, 2, 4-difluorobenzo nitril, 2, 5-difluorobenzo nitril, 2, 6-difluorobenzo nitril.

[0018] In addition, that will be easy to become unstable if extent of fluorination generally becomes large, and manufacture also becomes difficult, and since [ if it perfluoro-izes, ] it will further be easy to cause the fall of solubility, as for a nitryl compound, it is desirable to use mono-fluoro nitryl compounds, such as a fluoro acetonitrile, alpha-fluoro propionitrile, beta-fluoro propionitrile, 2-fluorobenzo nitril, 3-fluorobenzo nitril, and 4-fluorobenzo nitril. A fluoro acetonitrile, 2-fluorobenzo nitril, 3-fluorobenzo nitril, and 4-fluorobenzo nitril are more desirable especially.

[0019] The fluorinated nitryl compound can be used without using two or more kinds together, for example, separating isomer mixture with difficult separation. As for the fluorinated nitryl compound, it is desirable to occupy 0.01 - 10% of the weight of the electrolytic solution, and it is more desirable to occupy 0.1 - 5 % of the weight. If there are too few contents, coats enough on an electrode cannot be formed, but if many [ conversely / too ], the part which becomes coat generation with a surplus will have a bad influence on a cell property. In addition, various compounds in ordinary use can also be made to contain in the electrolytic solution in addition to the carbonate which makes the subject of an above-mentioned solvent, ester or the ether, a solute, and the fluorinated nitryl compound.

[0020] As an ingredient of a negative electrode, a metal lithium, and a lithium besides a lithium alloy will not be limited, especially if it is occlusion and the thing which may be emitted. For example, carbon materials, such as a pyrolysis object of the organic substance in various pyrolysis conditions, and an artificial graphite, a natural graphite, a metallic-oxide ingredient, etc. are mentioned.

[0021] It is desirable to use the artificial graphite manufactured among these by elevated-temperature heat treatment of the easy graphite pitch obtained from a carbon material, especially various raw materials, a purification natural graphite, or the graphite ingredient which performed various surface treatment which contains a pitch in these. It is desirable that d value (distance between layers) of the lattice plane (002nd page) for which it asked by the X diffraction by Gakushin method especially uses especially 0.335-0.34nm of things which are 0.335-0.337nm. As for a graphite ingredient, it is desirable to use what has few ash content, and ash content usually uses 1 or less % of the weight of a thing. It is desirable that the crystal size (Lc) for which ash content is especially 0.1 or less % of the weight, and asked by the X diffraction by Gakushin method 0.5 or less % of the weight uses a thing 30nm or more. Furthermore, as for microcrystal size (Lc), it is desirable that it is 50nm or more, and what is 100nm or more is the most desirable. Moreover, as for a graphite ingredient, it is desirable that the median size by the method of laser diffracting / being scattered about uses especially 1 micrometer - 100 micrometers of things which are 3 micrometers - 50 micrometers. It is most desirable that a median size uses especially 5 micrometers - 40 micrometers of things which are 7 micrometers - 30 micrometers. The BET adsorption method specific surface area of a graphite ingredient is usually 0.5m<sup>2</sup>/g-25.0m<sup>2</sup>/g, and is 0.7m<sup>2</sup>/g-20.0m<sup>2</sup>/g preferably. It is most desirable 1.0m<sup>2</sup>/g-15.0m<sup>2</sup>/g and that BET adsorption method specific surface area uses the thing of g-10.0m<sup>2</sup>/[ of 1.5m<sup>2</sup>/] g especially. Moreover, a graphite ingredient is set to the Raman spectrum

analysis which used Ar-ion-laser light. In the range of 1580-1620cm<sup>-1</sup>, Peak PA (peak intensity IA) And it has Peak PB (peak intensity IB) in the range of 1350-1370cm<sup>-1</sup>. And the intensity ratio R=IB/IA is 0-0.5, and with [ the full width at half maximum of the range of 1 or less / 26cm - / and 1350-1370cm<sup>-1</sup> ] one [ or less / 25cm - ], the full width at half maximum of the range of 1580-1620cm<sup>-1</sup> is still more desirable [ the full width at half maximum ].

[0022] Moreover, other negative-electrode material which emits [ occlusion and ] a lithium can also be mixed and used for these carbon materials. As occlusion and negative-electrode material which can be emitted, lithiums other than a carbon material Although metallic-oxide ingredients, such as metals, such as Ag, Zn, aluminum, Ga, In, Si, germanium, Sn, Pb, P, Sb, Bi, Cu, nickel, Sr, and Ba, an alloy of Li, or oxide of these metals, and a lithium metal are mentioned It is desirable to use Sn oxide, Si oxide, aluminum oxide, the RICHIMU alloy of Sn, Si, and aluminum, a metal lithium, etc. especially. Two or more kinds may be mixed and these negative-electrode ingredients may also be used.

[0023] What is necessary is just to perform manufacturing a negative electrode using these negative-electrode ingredients with a conventional method. For example, a binder, a thickener, electric conduction material, a solvent, etc. are added to a negative-electrode ingredient if needed, and it considers as the shape of a slurry, and this can be applied to the substrate of a charge collector and a negative electrode can be manufactured by drying. Moreover, roll forming of what added the binder etc. to the negative-electrode ingredient is carried out as it is, and it can consider as a sheet electrode or can also consider as a pellet electrode with compression molding.

[0024] As the binder used for manufacture of an electrode, a thickener, electric conduction material, etc., it is stable to the solvent used at the time of electrode manufacture, and to other ingredients used for the electrolytic solution and a cell, especially if it is a stable ingredient, it will not be limited. As a binder, polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, polyisoprene rubber, butadiene rubber, etc. are usually used.

[0025] Moreover, as a thickener, carboxyl methyl cellulose, methyl cellulose, a hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidization starch, phosphorylation starch, GAZEIN, etc. are usually used. As electric conduction material, conductive carbon materials, such as metallic materials, such as copper and nickel, graphite, and carbon black, are used. The point of metals, such as copper, nickel, and stainless steel, being used for the charge collector for negative electrodes, and being easy to process it into a thin film also in these, and the point of cost to copper foil is desirable.

[0026] As an ingredient of the positive electrode which constitutes the cell of this invention, lithium transition-metals multiple oxide ingredients, such as lithium cobalt oxide, a lithium nickel oxide, and a lithium manganic acid ghost, are usually used. A positive electrode can also be manufactured according to the manufacture approach of the above-mentioned negative electrode.

[0027] Metals, such as aluminum, titanium, and a tantalum, or the alloy of those is used for the charge collector for positive electrodes. Also in these, since especially aluminum or its alloy is lightweight, it is desirable in respect of energy density. The separator which isolates a negative electrode and a positive electrode is stable to the electrolytic solution, it is desirable to choose the solution retention outstanding thing, and it is desirable to use

a porous sheet or a nonwoven fabric etc. which uses polyolefines, such as polyethylene and polypropylene, as a raw material.

[0028] The nonaqueous electrolyte rechargeable battery concerning this invention can be manufactured with a conventional method except using the electrolytic solution containing the fluorinated nitryl compound. The configuration of a cell can also make the configuration of arbitration the coin type which carried out the laminating of the cylinder type, pellet electrode, and separator of the inside-out configuration which combined the cylinder type, pellet electrode, and separator which made the sheet electrode and the separator the shape of a spiral.

[0029]

[Example] Although an example and the example of a comparison are given to below and this invention is explained to it still more concretely, this invention is not limited to these examples, unless the summary is exceeded. In addition, the following performed the evaluation in production of a positive electrode, a negative electrode, and the coin mold cell using this, and a list.

[0030] Production of a positive electrode; 6 % of the weight of carbon black and polyvinylidene fluoride KF-1000(Kureha chemistry company make, trade name) 9 % of the weight were added to the LiCoO<sub>2</sub> 85% of the weight as positive active material, it mixed, the N-methyl-2-pyrrolidone was further added to this, and it considered as the shape of a slurry. This was applied to homogeneity on aluminium foil with a thickness of 20 micrometers which is a positive-electrode charge collector, and after desiccation, it pierced to discoid with a diameter of 12.5mm, and considered as the positive electrode.

[0031] d value of the lattice plane (002nd page) in an X diffraction Production of a negative electrode; 0.336nm, The median size according [ accord / microcrystal size (Lc) / 264nm / ash content ] to the method of laser diffracting / being scattered about 0.04% of the weight 17 micrometers, BET adsorption method specific surface area 8.9m<sup>2</sup>/g, In the Raman spectrum analysis using Ar-ion-laser light, it has the peak PA of the range of 1580-1620cm<sup>-1</sup> (peak intensity IA), and the peak PB (peak intensity IB) of the range of 1350-1370cm<sup>-1</sup>, and the intensity ratio R=IB/IA is 0.15. The styrene butadiene rubber made to distribute to the artificial-graphite powder KS-44 (TIMCAL, LTD. make, trade name) 94% of the weight whose full width at half maximum of the range of 1580-1620cm<sup>-1</sup> is 22.2cm<sup>-1</sup> with distilled water was added so that it might become 6 % of the weight by solid content. This was mixed by the De Dis parser, and it applied to homogeneity on copper foil with a thickness of 18 micrometers which is a negative-electrode charge collector, and after desiccation, what was made into the shape of a slurry was pierced to discoid with a diameter of 12.5mm, and was used as the negative electrode.

[0032] Production of a coin mold cel; the positive electrode was held in the can made from stainless steel which serves as a positive-electrode conductor, and the negative electrode was laid through the separator made from polyethylene which infiltrated the electrolytic solution on it. the obturation plate which serves both as this can and a negative-electrode conductor -- the gasket for an insulation -- minding -- it sealed in total and the coin mold cel was produced.

[0033] Evaluation of a coin mold cel; in 25 degrees C, the value which performed the charge and discharge test according to 0.5mA constant current by charge termination electrical-potential-difference 4.2V and discharge-final-voltage 2.5V, and broke the discharge capacity of a two-cycle eye by charge capacity of a two-cycle eye was defined

as two-cycle eye charge-and-discharge effectiveness. Moreover, after charging on the same conditions after a four cycle and saving at 85 degrees C in the state of charge for 72 hours, it was made to discharge and the value which broke the discharge capacity at this time by charge capacity of a four-cycle eye was defined as the preservation property.

[0034] It is example 1 capacity factor, and the fluoro acetonitrile was dissolved in the mixed liquor of ethylene carbonate:diethyl carbonate =1:1 so that it might become 2 % of the weight. LiPF<sub>6</sub> was dissolved in this so that it might become in l. and one mol /, and the electrolytic solution was prepared. In addition, under desiccation argon atmosphere, it fully dried and LiPF<sub>6</sub> was used.

[0035] It is example 2 capacity factor, and alpha-fluoro propionitrile was dissolved in the mixed liquor of ethylene carbonate:diethyl carbonate =1:1 so that it might become 2 % of the weight. LiPF<sub>6</sub> was dissolved in this so that it might become in l. and one mol /, and the electrolytic solution was prepared.

[0036] It is example 3 capacity factor, and 2-fluorobenzo nitril was dissolved in the mixed liquor of ethylene carbonate:diethyl carbonate =1:1 so that it might become 2 % of the weight. LiPF<sub>6</sub> was dissolved in this so that it might become in l. and one mol /, and the electrolytic solution was prepared.

[0037] It is example 4 capacity factor, and vinylene carbonate and a fluoro acetonitrile were dissolved in the mixed liquor of ethylene carbonate:diethyl carbonate =1:1 so that it might become 2 % of the weight, respectively. LiPF<sub>6</sub> was dissolved in this so that it might become in l. and one mol /, and the electrolytic solution was prepared.

[0038] LiPF<sub>6</sub> was dissolved in the mixed liquor which dissolved the fluoro acetonitrile in example 5 propylene carbonate so that it might become 2 % of the weight so that it might become in l. and one mol /, and the electrolytic solution was prepared.

[0039] It is example 6 capacity factor, and the fluoro acetonitrile was dissolved in the mixed liquor of ethylene carbonate:diethyl carbonate =1:1 so that it might become 2 % of the weight. LiBF<sub>4</sub> was dissolved in this so that it might become in l. and one mol /, and the electrolytic solution was prepared.

[0040] LiBF<sub>4</sub> was dissolved in the mixed liquor which dissolved the fluoro acetonitrile in example 7 gamma-butyrolactone so that it might become 2 % of the weight so that it might become in l. and one mol /, and the electrolytic solution was prepared.

[0041] LiPF<sub>6</sub> was dissolved in the mixed liquor which dissolved the fluoro acetonitrile in example 8 gamma-butyrolactone so that it might become 2 % of the weight so that it might become in l. and one mol /, and the electrolytic solution was prepared.

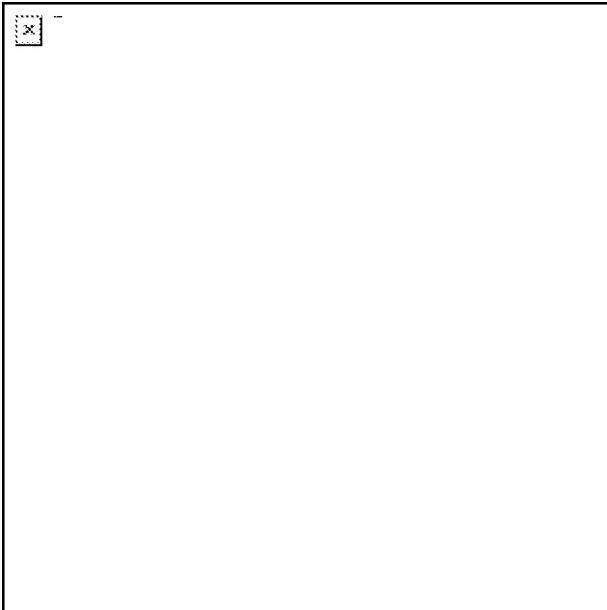
[0042] It was example of comparison 1 capacity factor, LiPF<sub>6</sub> was dissolved in the mixed liquor of ethylene carbonate:diethyl carbonate =1:1 so that it might become in l. and one mol /, and the electrolytic solution was prepared.

[0043] LiPF<sub>6</sub> was dissolved in example of comparison 2 propylene carbonate so that it might become in l. and one mol /, and the electrolytic solution was prepared.

[0044] LiBF<sub>4</sub> was dissolved in example of comparison 3 gamma-butyrolactone so that it might become in l. and one mol /, and the electrolytic solution was prepared.

[0045]

[Table 1]



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[Translation done.]

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